First-principles study on thermodynamical stability of metal borohydrides: Aluminum borohydride $Al(BH_4)_3$

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The thermodynamical stability of $Al(BH_4)_3$ has been investigated using first-principles calculations based on density functional theory. The heats of formation are obtained to be -132 and -131 kJ/mol without the zero-point energy corrections for α- and β-$Al(BH_4)_3$, respectively, which are made up of discrete molecular $Al(BH_4)_3$ units. It is predicted correctly that the α phase is more stable than the β phase. The energy difference between the solid phases and the isolated molecule is only about 10 kJ/mol. An analysis of the electronic structure also suggests the weak interaction between $Al(BH_4)_3$ molecules in the solid phases. It is confirmed that $Al(BH_4)_3$ obeys the linear relationship between the heat of formation and the Pauling electronegativity of the cation, which has been proposed in our previous study [Nakamori *et al.*, Phys. Rev. B **74**, 045126 (2006)].

I. INTRODUCTION

Metal borohydrides are potential candidates for hydrogen storage materials because of their high gravimetric density of hydrogen. Among borohydrides, alkali borohydrides such as $LiBH_4$ and $NaBH_4$ are well known and their properties have been investigated moderately.[1,2,3,4,5,6,7] Since these compounds are thermodynamically too stable and desorb hydrogen only at elevated temperatures, it is required to decrease their hydrogen desorption temperatures for practical applications. For $LiBH_4$, the reduction of the enthalpy change for the hydrogen desorption reaction has been attained by mixing with additives,[8,9,10] whose desorption temperatures are lower than that of pure $LiBH_4$ by a few hundreds kelvins.

Although borohydrides composed of non-alkali metals can be found in literature,[11] a little is known for their properties. In this context, we have recently investigated the thermodynamical stability of several metal borohydrides, $M(BH_4)_n$ (M = Li, Na, K, Cu, Mg, Zn, Sc, Zr, and Hf), both theoretically and experimentally.[12] It has been found that the stability of metal borohydrides shows a good correlation with the electronegativity of cations M. We have also determined the structural parameters experimentally for $Ca(BH_4)_2$ and its fundamental properties have been predicted theoretically.[13]

Aluminum borohydirde $Al(BH_4)_3$ is liquid at ambient temperatures with the melting point of 209 K. The structures of the solid phase have been investigated by x-ray diffraction measurements.[14] Cooling liquid $Al(BH_4)_3$, the orthorhombic β phase was initially grown and then the transition to the monoclinic α phase occurred at a temperatures in the range 180-195 K. In this study, we predict the thermodynamical stability of $Al(BH_4)_3$ and reexamine the correlation between the

stability of borohydrides and the cation electronegativity.

II. METHOD

The present calculations have been performed using the ultrasoft pseudopotential method[15] based on density functional theory.[16] The generalized gradient approximation[17] (GGA) is adopted for the exchange-correlation energy. The cutoff energies used in this study are 15 and 120 hartrees for the pseudowave functions and the charge density, respectively. The k-point grids for the Brillouin zone integration are generated so as to make the edge lengths of the grid elements as close to the target value of 0.08 bohr^{-1} as possible. These computational conditions give good convergence for the total energy within 1 meV/atom. The computational details can be found in Ref. 5 and the references therein.

III. RESULTS AND DISCUSSION

A. Thermodynamical stability of $Al(BH_4)_3$

The heat of formation for the following reaction is considered, that is, the formation of $Al(BH_4)_3$ from the elements:

$$Al + 3B + 6H_2 \rightarrow Al(BH_4)_3. \tag{1}$$
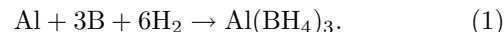
The heat of formation is estimated from the difference of the total energies between the left- and right-hand sides of Eq. (1). In this section, we ignore the zero-point energy (ZPE) contribution to the heat of formation.

The crystal structures of α- and β-$Al(BH_4)_3$ are shown in Figs. 1 (a) and (b), respectively. Both phases are
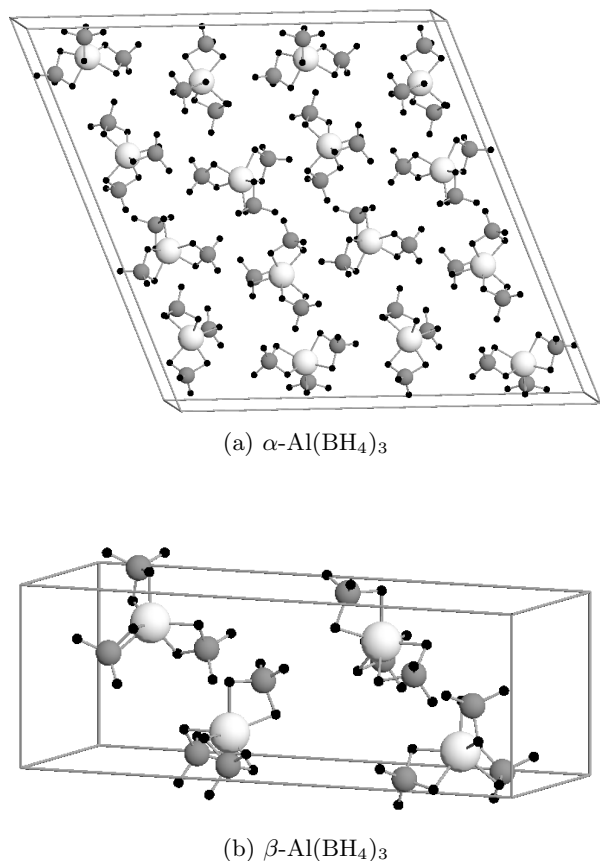
(a) α-Al(BH$_4$)$_3$

(b) β-Al(BH$_4$)$_3$

FIG. 1: Crystal Structure of (a) α- and (b) β-Al(BH$_4$)$_3$. White, gray, and black spheres indicate Al, B, and H atoms, respectively.

made up of discrete molecular Al(BH$_4$)$_3$ units in which three boron atoms form a planar AlB$_3$ skeleton and are bonded to Al atom by two bridging hydrogen atoms. The packing of the molecules is slightly denser in the α phase than in the β phase. The structural optimization is performed for both phases starting from the experimental configurations,[18,19] where the atomic positions as well as the lattice vectors are fully relaxed.

The optimized structural parameters are given in Tables I and II for α- and β-Al(BH$_4$)$_3$, respectively. The lattice constants are overestimated: The maximum deviation from the experimental values is 4 % for the a axis in the α phase and 6 % for the b axis in the β phase, which are larger than the errors of typical GGA calculations. The heats of formation are obtained as $\Delta H = -132$ kJ/mol for α-Al(BH$_4$)$_3$ and $\Delta H = -131$ kJ/mol for β-Al(BH$_4$)$_3$. It is predicted correctly that the α phase is more stable than the β phase.

The relatively large deviations found for the lattice constants are probably due to the weak interaction between molecular Al(BH$_4$)$_3$ units in the solid phases. The Al(BH$_4$)$_3$ molecules are expected to be neutral and not bonded strongly to each other. In this case, van
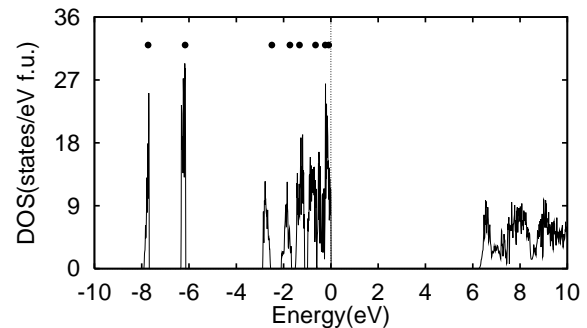

FIG. 2: Electronic density of states for α-Al(BH$_4$)$_3$. The origin of energy is set to be the top of valence states. The energy positions of the occupied states for molecular Al(BH$_4$)$_3$ are indicated by solid circles for comparison purpose.

der Walls interactions play an important role, which can not be described properly by the current GGA functional. To check this problem, we repeat the structural optimization, where the lattice constants are kept fixed at the experimental values and the atomic positions are only relaxed. The obtained heats of formation are -128 and -127 kJ/mol for the α and β phases, respectively. It can be confirmed that the relaxations of the lattice vectors give only a minor effect for the energetics of Al(BH$_4$)$_3$.

For comparison, the calculation is performed on molecular Al(BH$_4$)$_3$ which has D_3 symmetry. A hexagonal supercell with lattice constants of $a = c = 13.2$ Å is used with single Γ-point sampling. The heat of formation is predicted to be $\Delta H = -122$ kJ/mol. As expected, ΔH of molecular Al(BH$_4$)$_3$ is slightly higher than those of the solid states by about 10 kJ/mol. This small energy difference must be closely related to low melting point of Al(BH$_4$)$_3$. In Talbe III, we compare the bond lengths and angles obtained for molecular Al(BH$_4$)$_3$ with those for two solid phases. The geometries of Al(BH$_4$)$_3$ molecules are essentially unchanged when forming the solid phases. The agreement with the experimental data is good except for some of hydrogen related parameters. This is probably caused by the experimental difficulty in identifying H positions due to their weak x-ray scattering power.

Figure 2 depicts the electronic density of states for α-Al(BH$_4$)$_3$. The electronic structure is nonmetallic with a calculated gap of 6.0 eV. The occupied states consist of several sharp peaks whose energy positions correspond well to those of molecular Al(BH$_4$)$_3$. The similar correspondence can be found for β-Al(BH$_4$)$_3$. These also suggest the weak interaction between Al(BH$_4$)$_3$ molecules in the solid phases.

TABLE I: Optimized structural parameters for α-Al(BH$_4$)$_3$. Space group: $C2/c$ (No. 15). $a = 22.834$, $b = 6.176$ and $c = 22.423$ Å, and $\beta = 111.67°$. The unit cell contains two independent Al(BH$_4$)$_3$ molecules. The experimental lattice parameters are $a = 21.917$, $b = 5.986$ and $c = 21.787$ Å, and $\beta = 111.90°$.[14,18]

	Wyckoff position	coordinates				Wyckoff position	coordinates		
		x	y	z			x	y	z
Al	8f	0.3797	0.5943	0.8366	Al	8f	0.3659	0.1127	0.5947
B1	8f	0.3205	0.3121	0.8239	B1	8f	0.3626	−0.1633	0.5349
H1$_a$	8f	0.3809	0.3078	0.8439	H1$_a$	8f	0.3860	−0.1645	0.5965
H1$_b$	8f	0.3002	0.5071	0.8128	H1$_b$	8f	0.3437	0.0276	0.5138
H1$_c$	8f	0.3067	0.2479	0.8677	H1$_c$	8f	0.3163	−0.2759	0.5191
H1$_d$	8f	0.3019	0.2214	0.7725	H1$_d$	8f	0.4058	−0.2032	0.5180
B2	8f	0.3899	0.7542	0.7555	B2	8f	0.2793	0.2182	0.6028
H2$_a$	8f	0.4165	0.5751	0.7794	H2$_a$	8f	0.3147	0.0676	0.6368
H2$_b$	8f	0.3516	0.8141	0.7820	H2$_b$	8f	0.3067	0.3176	0.5703
H2$_c$	8f	0.3575	0.7139	0.7005	H2$_c$	8f	0.2749	0.3494	0.6407
H2$_d$	8f	0.4309	0.8894	0.7685	H2$_d$	8f	0.2332	0.1306	0.5652
B3	8f	0.4298	0.7324	0.9297	B3	8f	0.4542	0.2773	0.6427
H3$_a$	8f	0.3703	0.7520	0.8985	H3$_a$	8f	0.4187	0.3056	0.5838
H3$_b$	8f	0.4541	0.6038	0.9002	H3$_b$	8f	0.4282	0.1495	0.6705
H3$_c$	8f	0.4349	0.6401	0.9787	H3$_c$	8f	0.4573	0.4508	0.6683
H3$_d$	8f	0.4531	0.9080	0.9304	H3$_d$	8f	0.5010	0.1867	0.6426

TABLE II: Optimized structural parameters for β-Al(BH$_4$)$_3$. Space group: $Pna2_1$ (No. 33). $a = 18.649$, $b = 6.488$ and $c = 6.389$ Å. The unit cell contains one independent Al(BH$_4$)$_3$ molecule. The experimental lattice constants are $a = 18.021$, $b = 6.138$ and $c = 6.199$ Å.[14,19]

	Wyckoff position	coordinates		
		x	y	z
Al	4a	0.8703	0.1558	0.2098
B1	4a	0.7800	0.0057	0.0633
H1$_a$	4a	0.8456	−0.0341	0.0213
H1$_b$	4a	0.7751	0.1384	0.2112
H1$_c$	4a	0.7552	−0.1515	0.1331
H1$_d$	4a	0.7551	0.0858	−0.0906
B2	4a	0.9168	0.0183	0.4855
H2$_a$	4a	0.9353	−0.0248	0.2979
H2$_b$	4a	0.8712	0.1661	0.4885
H2$_c$	4a	0.9700	0.0865	0.5674
H2$_d$	4a	0.8870	−0.1319	0.5547
B3	4a	0.9115	0.4349	0.0722
H3$_a$	4a	0.8623	0.4281	0.2121
H3$_b$	4a	0.9337	0.2529	0.0277
H3$_c$	4a	0.9619	0.5214	0.1520
H3$_d$	4a	0.8837	0.5009	−0.0844

B. Correlation between stability of borohydrides and cation electronegativity

In Ref. 12, we have found a good correlation between the heat of formation ΔH and the Pauling electronegativity of the cation χ_P, when ΔH is normalized by the number of BH$_4$ complexes in the formula unit. This correlation can be represented by the linear relationship, $\Delta H = 248.7\chi_P - 390.8$ in the unit of kJ/mol BH$_4$. In this section, we refine this relation using the additional results for α-Al(BH$_4$)$_3$ and Ca(BH$_4$)$_2$.[13]

In order to estimate the ZPE contribution to ΔH for Al(BH$_4$)$_3$, the normal eigenmode frequencies are calculated for molecular Al(BH$_4$)$_3$. The weak interaction between Al(BH$_4$)$_3$ molecules in the solid phases justifies this treatment. The result is shown in Fig. 3, where the obtained frequencies agree fairly well with the results of the experiment[20] and the quantum chemistry calculation.[21] The ZPE contribution to ΔH is predicted to be 36 kJ/mol BH$_4$. This value is quite close to the approximated value of 33 kJ/mol BH$_4$ adopted in Ref. 12, which has been obtained using the molecular approximation for a [BH$_4$]$^-$ anion. To keep the consistency with the previous treatment, we decide to use the approximated value of 33 kJ/mol BH$_4$, where the normalized heats of formation with the ZPE correction become −11 and −155 kJ/mol BH$_4$ for Al(BH$_4$)$_3$ and Ca(BH$_4$)$_2$, respectively.

In Fig. 4, the normalized heat of formation ΔH with the ZPE correction as a function of the Pauling electronegativity of the cation χ_P is plotted.[22] It can

TABLE III: Comparison of the bond lengths d (Å) and angles θ (°) obtained for molecular $Al(BH_4)_3$ and two solid phases. For d(Al-H) and θ(H-Al-H), H atoms forming the bridge bond are only cosidered.

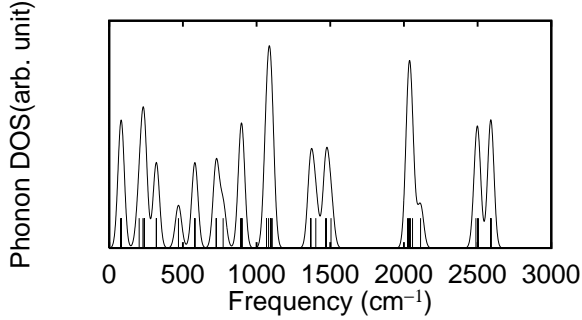|	Calc.			Expt.[a]	
	molecule	α phase	β phase	α phase	β phase
d(Al-B)	2.16	2.15-2.16	2.15-2.16	2.10-2.14	2.10-2.13
d(Al-H)	1.77	1.77-1.78	1.77-1.78	1.73-1.76	1.68-1.75
d(B-H)	1.20-1.29	1.20-1.29	1.21-1.28	0.99-1.14	0.99-1.14
θ(B-Al-B)	120	117-122	119-122	119-121	119-123
θ(H-Al-H)	73	73	73	65	63-65
θ(H-B-H)	106-122	105-121	105-121	103-121	106-130

[a]Reference 14.

FIG. 3: Normal eigenmode frequencies for molecular $Al(BH_4)_3$. The calculated frequencies are indicated by vertical bars and the Gaussian broadening with a width of 30 cm^{-1} is used.

be found that the results for $Al(BH_4)_3$ and $Ca(BH_4)_2$ also obey the linear relationship. The least square fitting yields

$$\Delta H = 253.6\chi_P - 398.0, \qquad (2)$$

with an absolute mean error of 9.6 kJ/mol BH_4. The addition of two new data points causes only a little change in the coefficients for the linear relation. The present study provides the additional support for the linear correlation between ΔH and χ_P. The Pauling electronegativity of the cation χ_P is a good indicator to estimate the thermodynamical stability of borohydrides.

IV. CONCLUSIONS

In this study, we have predicted the thermodynamical stability of $Al(BH_4)_3$ and reexamined the correlation between the stability of borohydrides and the cation electronegativity.

The heats of formation are obtained as -132 and -131 kJ/mol without the zero-point energy corrections for α- and β-$Al(BH_4)_3$, respectively, which are made up of discrete molecular $Al(BH_4)_3$ units. It is correctly
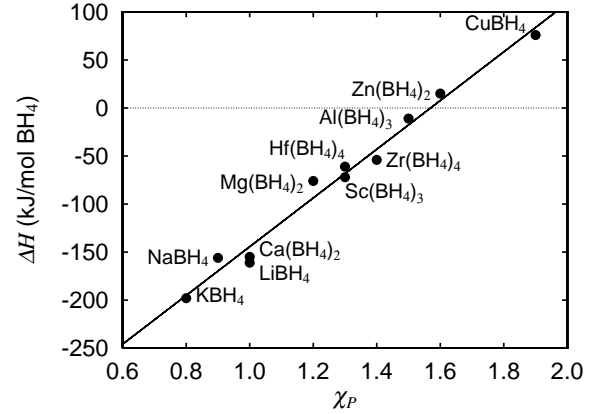

FIG. 4: Relation between the heat of formation ΔH and the Pauling electronegativity of the cation, χ_P. The straight line indicates the result of the least square fitting, $\Delta H = 253.6\chi_P - 398.0$. The zero-point energy contributions to ΔH are approximately taken into consideration (see the text).

predicted that the α phase is more stable than the β phase. The energy difference between the solid phases and the isolated molecule is small and the interaction between the molecules in the solid phases is expected to be weak. This is most likely related to low melting point of $Al(BH_4)_3$.

The linear correlation between the heat of formation and the Pauling electronegativity of the cation, which has been proposed in the previous study,[12] is also held for $Al(BH_4)_3$ as well as for $Ca(BH_4)_2$. The Pauling electronegativity of the cation is a good indicator to estimate the thermodynamical stability of borohydrides.

[1] A. Züttel, P. Wenger, S. Rentsch, P. Sudan, Ph. Mauron, and Ch. Emmenegger, J. Power Sources **118**, 1 (2003).

[2] Y. Kojima and T. Haga, Int. J. Hydrogen Energy **28**, 989 (2003).

[3] G. Renaudin, S. Gomes, H. Hagemann, L. Keller, and K. Yvon, J. Alloys Compd. **375**, 98 (2004).

[4] S. Orimo, Y. Nakamori, G. Kitahara, K. Miwa, N. Ohba, S. Towata, and A. Züttel, J. Alloys Compd. **404-406**, 427 (2005).

[5] K. Miwa, N. Ohba, S. Towata, Y. Nakamori, and S. Orimo, Phys. Rev. B **69**, 245120 (2004).

[6] N. Ohba, K. Miwa, M. Aoki, T. Noritake, S. Towata, Y. Nakamori, S. Orimo, and A. Züttel, Phys. Rev. B **74**, 075110 (2006).

[7] S. Orimo, Y. Nakamori, N. Ohba, K. Miwa, M. Aoki, S. Towata, and A. Züttel, Appl. Phys. Lett. **89**, 021920 (2006).

[8] M. Aoki, K. Miwa, T. Noritake, G. Kitahara, Y. Nakamori, S. Orimo, and S. Towata, Appl. Phys. A: Mater. Sci. Process. **80**, 1409 (2005).

[9] F. E. Pinkerton, G. P. Meisner, M. S. Meyer, M. P. Balogh, and M. D. Kundrat, J. Chem. Phys. B **109**, 6 (2005).

[10] J. J. Vajo, S. L. Skeith, and F. Mertens, J. Phys. Chem. B **109**, 3719 (2005).

[11] For example, E. A. Sullivan and R. C. Wade, Kirk-Othmer Encyclopedia of Chem. Tech. 1980, Vol. 12, p.772.

[12] Y. Nakamori, K. Miwa, A. Ninomiya, H. Li, N. Ohba, S. Towata, A. Züttel, and S. Orimo, Phys. Rev. B **74**, 045126 (2006).

[13] K. Miwa, M. Aoki, T. Noritake, N. Ohba, Y. Nakamori, S. Towata, A. Züttel, and S. Orimo, Phys. Rev. B **74**, 155122 (2006).

[14] S. Aldridge, A. J. Blake, A. J. Downs, R. O. Gould, S. Parsons, and C. R. Pulham, J. Chem. Soc, Dalton Trans. 1007 (1997): The full list of the structural parameters for α- and β-Al(BH$_4$)$_3$ is available at the Cambridge Crystallographic Data Center (www.ccdc.cam.ac.uk) with the deposition number 186/404.

[15] D. Vanderbilt, Phys. Rev. B **41**, 7892 (1990); K. Laasonen, A. Pasquarello, R. Car, C. Lee, and D. Vanderbilt, *ibid.* **47**, 10142 (1993).

[16] P. Hohenberg and W. Kohn, Phys. Rev. **136**, B864 (1964); W.Kohn and L. J. Sham, *ibid.* **140**, A1133 (1965).

[17] J. P. Perdew, K. Burke, and M. Ernzerhof, Phys. Rev. Lett. **77**, 3865 (1996); **78**, 1396(E) (1997).

[18] Cambridge Crystallographic Data Center: CCDC No. 230830.

[19] Cambridge Crystallographic Data Center: CCDC No. 230829.

[20] D. A. Coe and J. W. Nibler, Spectrochim. Acta **29A**, 1789 (1973).

[21] J. O. Jensen, Spectrochim. Acta **59A**, 1565 (2003).

[22] We recalculate ΔH for Mg(BH$_4$)$_2$ using the crystal structure proposed by Vajeeston *et al.* [Appl. Phys. Lett. **89**, 071906 (2006)]. The obtained ΔH is -109 kJ/mol BH$_4$ without the ZPE correction, which is slightly lower than the value of -104 kJ/mol BH$_4$ reported in Ref. 12.